Indian J. Phys. **51B**, 178-183 (1977)

Electronic spectra of styrene and its derivatives

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The electronic spectra of styrene and some of its derivatives have been examined, the electronic shift (the 0,0 band shift) as well as the excited states of styrene have been discussed in terms of conjugation of vinyl ($-CH=CH_2$) and phenyl ($-C_6H_5$) groups. The directivity of vinyl group has also been compared with other substituent groups.

1. INTRODUCTION

Styrene possesses highly reactive double bond and resembles greatly with benzaldehyde, benzonitril and benzoic acid in its unsaturation, but differs in electron accepting power. The vinyl group in styrene is isoelectronic with $-N=N-$ (aza), carbonyl and nitroso groups but does not contain any hetero-atoms like O, N or S. Comparison of he ionisation potential of styrene with those of phenol, toluene, chlorobenzene, bromobenzene etc. suggests that styrene should have ortho-para directivity. Further, a consideration of the interactions between the highest occupied and the lowest vacant orbitals of benzene and the substituent groups (Nagakura & Tanaka 1954) shows that it is difficult to determine the exact nature of migration of electron between the vinyl and phenyl groups in styrene i.e. vinyl group is neither regarded as a donor (ortho-para directing) nor an acceptor (meta directing). It is quite possible that this group has both donor and acceptor properties to an equal degree (Murrell 1963). These inherent properties attach a unique spectral feature to styrene, its electronic states and the geometry.

It is, therefore, worthwhile to examine and compare the electronic spectra of styrene and its derivatives, in brief, the vibronic structures of which have recently been published by author and a few more workers (Ansari *et al* 1967, Ansari 1968, Ansari & Sharma 1968, Ansari & Singh 1971, Tripathi 1967, 1968; Robertson et al 1950, Margan 1953, Singh 1966, Shukla 1972) and discuss the electronic shift, styrene states and its geometry.

2. ELECTRONIC SPECTRA

Four π-electronic transitions have been reported in styrene and the excitation energies pertaining to these various states computed theoretically (Coulson &

Streitwieser 1965, Platt 1950) and a fair correlation has been established with experimental data. Thus like aniline styrene also exhibits an additional band system as compared to benzene. The spectra of styrene has been interpreted on localized orbital model (Longuet-Higgins & Murrell 1955, Platt 1950) and one finds that the first band system λ 2800 (ε=700) is essentially an excitation within the benzene ring while the second λ 2460 (ε=15,000) is a strong mixture of the B_{1u} state and charge transfer (CT) states. The origin of the third λ 2030 (ε=23,000) and fourth λ 1730 (ε=2,000) is not very well understood. These are, however, excitations between the CT states.

The electronic spectra of styrene molecule have been recorded by a number of workers in liquid as well as vapour phase (Ramart-Lucas & Amagat 1932, Margan 1953, Nikitana 1953, Robertson et al 1950, Sen 1956, Singh 1966). The first attempt for the vibrational analysis of the longest wavelength system was due to Robertson et. al. They measured about 400 bands in the vapour absorption and could decipher only four excited state frequencies (746, 948, 959 and 1209 cm^{-1}). Later Margan (1953) has reinvestigated the absorption and fluorescence spectra of this molecule and identified a few more excited state frequencies (148, 478, 1024, 1300 and 1486 cm^{-1}). From a comparison and correlation of the longest wavelength system with those of mono-substituted ethylenes (particularly with butadiene), Robertson et. al. attributed the band system to an analogue of $B_{1u} \leftarrow A_{1g}$ system of benzene, which may remove the contraversial opinion and assignment of the system as K-band by Klevens & Platt (1949) and Platt (1950).

The absorption spectra of substituted styrenes (Ansari et. al. 1967, Ansari 1968, Ansari & Sharma 1968, Ansari & Singh 1971, Tripathi 1967, 1968, Shukla 1972) consist of two separate electronic transitions : one weak discrete system and other strong continuous system. No sharp demarkation between these two transitions can be inferred from the inspection of the spectrograms. The longer wavelength end of the continuous absorption seems to superimpose the shorter region of the discrete system and extends towards longer wavelength system covering the entire discrete system at higher vapour pressures limiting the further extension of more bands towards long wavelength side of the 0,0 band. However, in the case of fluorostyrenes (Ansari *et. al.* 1957, Tripathi 1967) a few more bands have been observed towards the long wavelength side of the 0,0 band at higher vapour pressures and longer absorbing paths. The bands, in general, are sharp and degraded to red in ortho-and meta isomers of fluorostynene (Ansari *et. al.* 1967, Tripathi 1967) Chlorostyrene (Tripathi 1968), bromostyrene (Ansari 1968) and methylstyrene (Ansari and Sharma 1968), whereas in the para-isomers the bands are narrow but somewhat diffuse. In the case of dichlorostyres (Ansari & Singh 1971) and 1,3-divinylbenzene (Shukla 1972), the bands are also sharp and degraded to red. This discrete system in each of the substituted styrenes resembles greatly that of styrene in intensity, vibrational structure and region of absorption, and can be attributed to benzenoid origin.

While proposing the vibrational analysis Robertson et. al. assumed the moleculer plane of styrene as the only symmetry element as the axis of the vinyl C=C double bond does not coincide with the para—axis of styrene. In addition to the excitation of various benzene vibrations, (which will not be discussed here for brevity), they and Margan 1953 deciphered the excitation of two excited state frequencies 1209 and 1484 cm^{-1} involving a strong conjugation of the vinyl group with the benzene ring. They assigned the former due to C-vinyl stretching and the latter due to vinyl C=C stretching. The C—vinyl stretching is invariably observed around 1200 cm^{-1} and the magnitude does not change appreciably in ground state (infrared or Raman value) even in the case of substituted styrenes (Table 1). Some increase in the

Table 1. C-vinyl and vinyl C=C stretchings in styrene and its derivatives (All values are in cm^{-1})

Molecules	C- (CH=CH_2) Stretching		C=C Stretching	
Styrene	1209	(1204)	1484	(1628)
0-Fluorostyrene	1198	(1202)	—	(1630)
m-Fluorostyrene	—	(1204)	—	(1628)
p-Fluorostyrene	1202	(1204)	1447	(1632)
o-Chlorostyrene	1198	(1209)	1440	(1629)
m-Chlorostyrene	1206	(1204)	1417	(1632)
p-Chlorostyrene	1198	(1200)	1440	(1632)
o-Bromostyrene	1175	(1205)	—	(1625)
m-Bromostyrene	1203	(1205)	1408	(1625)
p-Bromostyrene	1195	(1202)	1437	(1628)
o-Methylstyrene	1207	(1220)	1424	(1625)
m-Methylstyrene	1203	(1220)	1412	(1630)
p-Methylstyrene	1190	(1205)	1431	(1630)
2,5-Dichlorostyrene	1217	(1195)	1406	(1620)
3,4-Dichlorostyrene	1217	(1198)	—	(1623)

Values in parentheses are Raman or infrared frequencies taken from (i) Pitzer et al 1946 (Styrene), (ii) Tripathi 1968 (fluorostyrenes & chlorostyrenes) (iii) Ansari 1968, 1970 (bromostyrenes & methylstyreses) (iv) Ansari & Singh 1971 (dichlorostyrenes).

magnitude of the excited state frequency as compared to ground state frequency has been observed, which suggests that C-vinyl bond goes under a little constrain in the excited state. While the value of vinyl C=C stretching is markedly reduced to 1484 cm^{-1} in styrene and around 1425 cm^{-1} in substituted styrenes (ground state value $\approx$ 1630 cm^{-1}). This depression is accounted by the lesser conjugation of the vinyl group with phenyl ring in the excited state

It is believed that in the excited state, the molecules no longer remained of planar configuration (deviation from the coplanarity in excited state) and the C=C bond rests to an increased value (lengthening in the bond), while C-vinyl bond goes to a little constrain. This is why the C-vinyl stretching in the excited state is of somewhat higher value as compared to ground state value. However, this constrain is negligible to the lengthening in C=C bond. Further, from a correlation of the degree of conjugation of the C=C double bond (of the vinyl group) with the benzene ring, i.e., the delocalisation of the π-electrons of the latter and the disposition of the substituents Pao-Shan *et. al* (1962) have pointed out that the conjugation is enhanced in para-substituted styrenes, while it is reduced in ortho-and multisubstituted styrenes. This is in confirmation with the experimental observation that the electronic spectra of ortho- and para-isomers, and multi substituted styrenes are alike whereas they differ with para-isomers (vide supra).

3. Electronic Shift

The vinyl group, in styrene, shifts the benzene spectrum to about 3328 cm $^{-1}$ (table-2) and this large bathochromic shift is attributed due to conjugation of this group with phenyl group. Substitution of one or more basic groups, further, adds electronic and or steric interactions to styrene states resulting in the consequent intensifications and further wavelength shifts. In disubstituted benzenes, having one donor and the other acceptor substituents or groups, Merrell (1963) has pointed out that the spectra of ortho- and meta-substituted compounds are similar to one another but different from those of the para compounds (vide supra). Moreover, it is the ortho- and meta compounds which absorb at the longer wavelengths. A semi-empirical account of these experimenal regularities has been given by Chandra and Tripathi (1963). If both substituents are ortho para-directing or meta-directing, the order of the red shift of the 0,0 band is ortho $<$ meta $<$ para reverse is the case when one is ortho-para-directing and the other is meta-directing. The well known nature of migration of electrons in halogens and methyl group i.e. ortho-para-directing property, and the order of the red shifts (ortho$>$ meta$>$para) of chloro-, bromo- and methylstyrenes with respect to that of benzene suggest that vinyl group in styrene may have somewhat meta-directing i.e. ortho-para-directing property, and the other order of the red shifts (ortho$>$ may be accounted for by the high electronegativity of fluorine atom. It is to be concluded that the resultant of electronic and steric parturbations is predominent in the same order.

It is also noteworthy that the 0,0 band shift for meta isomers of fluoro-chloro-, bromo-, methyl-styrenes and meta-divinyl benzene appears to obey the additive rule. The sum of the 0,0 band shift of styrene and corresponding monosubstituted benzenes are remarkably close to the observed shifts in meta-isomers. (table-2).

Table 2. The 0,0 band shifts in styrene and its derivatives
(All values are in cm^{-1})

Molecules	0,0 band	shift w.r.t. Benzene	Red shift order	Additive shift	Error in Experimental and calculated value*
Benzene	38089	0			
Styrene	34761	3328			
F-Benz.	37819	270			
o-FS	34343	3746			
m-FS	34405	3684	p > o > m	3598	2.3%
p-FS	34315	3774			
C-Benz.	37052	1037			
o-CS	33582	4507			
m-CS	33762	4327	o > m > p	4365	0.9%
p-CS	33979	4110			
B-Benz	36996	1093			
o-BS	33559	4530			
m-BS	33719	4370	o > m > p	4421	1.1%
p-BS	33963	4126			
Toluene	37475	614			
o-MS	33909	4180			
m-MS	34127	3962	o > m > p	3942	0.5%
p-MS	34279	3810			
1,3 DVB	31419	6670		6656	0.1%

*for meta-isomers only
(Fluorobenzene—Wollmann 1946, Chlorobenzene—Sponer & Wollmann 1941, Bromobenzene—Prakash 1949-63, Toluene—Ginsberg et. al. 1946).

References

1. Ansari B. J., Sharma D. & Tripathi G. N. R. 1967. Ind. J. Pure Appl. Phys. **5**, 187.
2. Ansari B. J. 1968. Ind. J. Pure Appl. Phys. **6**, 49.
3. Ansari B. J. 1968. Ind. J. Pure Appl. Phys. **6**, 614.
4. Ansari B. J. & Singh I. D. 1971 Technology **8**, 253.
5. Ansari B. J. 1968. Ind. J. Pure Appl. Phys. **6**, 89.
6. Ansari B. J. 1970 Ind. J. Pure Appl. Phys. **8**, 725
7. Chandra K. & Tripathi G. N. R. 1963 *Proceedings of the Symposium on Spectroscopy and Allied problems held under the auspices of C.S.I.R.*, New Delhi, 122.
8. Coulson C. A. & Streitwieser Jr. A. 1965 *Dictionary of π-Electron calculations* (W. H. Freeman & Co., San Francisco) 8.
9. Ginsberg N., Robertson W. W. & Matsen F. A. 1964 J. Chem. Phys. **14**, 516.

10. Klevens H. B. & Platt J. R. 1949 J Amer. Chem. Soc. **71**, 1710
11. Longuet-Higgins H. C. & Murrell J. N. 1955 Proc. Phys. Soc. **A68**, 601
12. Margan J. V. 1953 J. Am. Chem Soc. **75**, 5055.
13. Murrell J. N. 1963 *The Theory of the Electronic Spectra of Organic Molecules* (Methuen, London).
14. Nagakura S. & Tanaka J. 1954 J. Chem Phys. **22**, 236.
15. Nikitana A N. 1953 Acid. Sci., U.S.S.R., Fiz. **17**, 728.
16. Pao-Shan, Yu, Nikitin V. N. & Vol' kenshtein M. V. 1962. Zh. Fiz. Khim **36**, 356
17. Pitzer K. S., Guttman L. & Westrum E. F. (Jr.) 1946 J. Amer Che. Soc. **68**, 2209
18. Platt. J. R. 1950 J. Chem. Phys. **18**, 1168.
19. Prakash S. 1949-63 B H.U. Research Report
20. Ramart-Lucas. P. & Amagat P. 1932 Bull. Soc. Chim, France **51**, 965
21. Robertson. W. W., Music J. F. & Matsen F A. 1950. J. Amer. Chem. Soc. **72**, 5260
22. Sen S. K. 1956 Ind. J. Phys. **30**, 321.
23. Shukla M. M. 1972 Ph.D. Thesis, Gorakhpur University
24 Singh. R. N. 1966 Ind. J. Pure Appl. Phys. **4**, 1
25. Spiner H. & Wollmann S. H. 1941 J. Chem. Phys. **9**, 816.
26. Tripathi G. N. R. 1967 Ind. J. Pure Appl. Phys **5**, 189
27. Tripathi G. N. R. 1968 Ph.D. Thesis Gorakhpur University
28. Tripathi L. N. & Tripathi G. N. R. 1967 *Proc. of the International Conference on Spectroscopy* (B.A.R.C.) Bombay II. 298
29. Wollmann S. H. 1946 J Chem. Phys **14**, 123